

# The Crystal Structure of the Intermetallic Compound $\text{ZrZn}_{22}$ \*

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A complete determination of the crystal structure of the binary intermetallic compound most rich in zinc, the  $\xi$ -phase, in the zirconium–zinc system has been carried out with use of all intensity data obtainable from single crystal Weissenberg photographs taken with  $\text{Cu } K\alpha$  radiation. The composition of the completely ordered phase is  $\text{ZrZn}_{22}$ . The refinement of the structure was carried out by application of the method of least-squares. The space group is  $O_h^7\text{-}Fd\bar{3}m$  with 184 atoms per unit cube. The edge of the cubic unit cell determined with use of powder samples was  $a_0 = 14.101 \pm 0.002 \text{ \AA}$ . The truncated tetrahedron, the icosahedron, and the hexagonal prism are prominent coordination polyhedra in this structure. An analysis of these polyhedra reveals that the packing of atoms around the crystallographically different zinc atoms varies widely.

## Introduction

In his examination of a series of zirconium–zinc alloys Pietrokowsky (1958) observed a binary intermetallic compound very rich in zinc. Rotation and Weissenberg photographs showed this phase to be cubic with the edge of the unit cell approximately equal to  $14 \text{ \AA}$ . The exact composition was not known. His photographs were found on direct comparison to be very similar to those obtained by me from crystals of the  $\text{Mg}_3\text{Cr}_2\text{Al}_{18}$  phase, also cubic with  $a_0 = 14.53 \text{ \AA}$ . Dr. Pietrokowsky very kindly left to me the further prosecution of this work.

While the present investigation was in progress no reports on intermediate zirconium–zinc phases other than those on the  $\text{ZrZn}$  phase (Gebhardt, 1941) and the  $\text{ZrZn}_2$  phase (Pietrokowsky, 1954) were found in the literature. However, recently a paper was published by Chiotti and Kilp (1959), who reported the composition of the above-mentioned phase to correspond approximately to the formula  $\text{ZrZn}_{14}$ . These authors also reported that the edge of the cubic unit cell is  $a_0 = 14.11 \text{ \AA}$  and that the probable space group is  $Fd\bar{3}m$ , but they did not determine the positions of the atoms.

## Experimental work

### Single crystals

A series of binary zirconium–zinc alloys were prepared by melting together pieces of the pure metals in alundum crucibles by induction heating in argon gas at atmospheric pressure. The melts were allowed to solidify slowly at varying cooling rates.

One of the samples that contained approximately five percent by weight of zirconium expanded on solidification to a voluminous and brittle mass

containing a vast number of very regularly shaped octahedral crystals. This alloy will hereafter be referred to as sample no. 1.

The materials used in these preparations as well as in those described below were Baker & Adamson reagent grade granulated zinc of 99.98% purity and hafnium-free iodide-process zirconium.

### Composition and density

Thirty-four milligrams of octahedral crystals were manually selected under a binocular microscope from sample no. 1. A complete chemical analysis of these crystals gave 9.2% Zr and 90.8% Zn. This composition corresponds to the formula  $\text{ZrZn}_{13.6}$  in good agreement with the result obtained by Chiotti & Kilp (1959).

Since the quantity of single crystals available was not sufficient to yield density measurements of desired accuracy, attempts were made to prepare a single-phase alloy of the composition  $\text{ZrZn}_{14}$ ; alloys containing more than approximately five percent of zirconium were, however, segregated even though they were prepared by rapid solidification of the melt.

When the equilibrium diagram by Chiotti & Kilp (1959) became available, a new method for separation of a single-phase alloy was devised on the basis of their thermal data. The procedure was as follows.

A melt containing approximately five percent of zirconium by weight was heated to about  $900^\circ\text{C}$  in an alundum crucible under argon gas at atmospheric pressure. The melt was vigorously stirred with an aluminum oxide rod and then rapidly transferred into a heavy, cylindrical copper mould. The pouring temperature was kept well above the liquidus temperature, which is for this composition about  $700^\circ\text{C}$ . Evaporation of some zinc could be tolerated for reasons that soon will become obvious. The cylindrical ingot obtained was one-quarter of an inch in diameter and two inches long. It was annealed for a few days at  $350^\circ\text{C}$  in an evacuated and sealed Pyrex tube.

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Subsequently the tube was placed at about  $45^\circ$  to the horizontal and the temperature was raised to  $500^\circ\text{C}$ , i.e. about  $84^\circ\text{C}$  above the melting point of the eutectic, located at about 99.7% Zn, and  $45^\circ\text{C}$  below the peritectic dissociation temperature of the compound. The sample, now liquid+compound, was left in this environment for 1700 hours. During this time the liquid separated from the intermetallic compound and collected in the bottom of the tube.

A photomicrograph taken from a polished and etched section of the upper part of the ingot showed, as expected, only one phase. This part was separated and broken up into chips which will be referred to as sample no. 2. The powder diffraction pattern obtained by using grindings of this sample was identical with that obtained from a powder prepared by crushing octahedral crystals isolated from sample no. 1. No foreign lines could be detected on the clear intense photograph of sample no. 2.

The density of sample no. 2 was found to be  $7.15 \pm 0.05 \text{ g.cm}^{-3}$  by use of a displacement method, where the uncertainty refers to the standard deviation of three measurements.

It was now divided into two approximately equal parts, which were chemically analyzed at two different commercial laboratories. The results were as follows:

1. Zr 6.00%, Zn 93.95%; i.e.,  $\text{ZrZn}_{21.8}$ .
2. Zr 6.46%, Zn 93.68%; i.e.,  $\text{ZrZn}_{20.4}$ .

A semiquantitative spectroscopic analysis showed in addition the presence of 0.05% copper but no trace of hafnium.

#### Unit-cell edge

Powder photographs were taken with nickel-filtered  $\text{Cu } K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) in a camera of 5 cm. radius with the film placed in the asymmetric position. The edge of the cubic unit cell as determined by the extrapolation method of Nelson & Riley (1945) was  $a_0 = 14.103 \pm 0.001 \text{ \AA}$  for sample no. 1 and  $a_0 = 14.101 \pm 0.002 \text{ \AA}$  for sample no. 2.

#### Space group

Octahedral crystals isolated from sample no. 1 were used for the subsequent single-crystal work.

All diffraction patterns obtained with copper radiation from these crystals were almost identical with those observed for the  $\text{Mg}_3\text{Cr}_2\text{Al}_{18}$  phase, the probable space group of which was found to be  $O_h^7\text{-}Fd\bar{3}m$  (Samson, 1958). However, the heavily exposed zero-layer Weissenberg photographs with the crystal rotated about [001] showed five very weak spots corresponding to the reflections 600, 10.0.0, 420, 820, and 14.4.0 not consistent with the space group  $O_h^7\text{-}Fd\bar{3}m$ .

Additional Weissenberg photographs were taken using  $\text{Cu } K\alpha$  radiation with the crystal rotated about [011]. On the zero-layer photograph a spot corresponding to the 600 reflection was again observed, but it

was here considerably more intense than on the above-mentioned photograph, while a spot corresponding to 10.0.0 was considerably fainter than before. On the third-layer photograph a spot corresponding to the 060 reflection was also recorded, but it was here extremely faint. No reflections corresponding to 042, 0.4.14, and 082 occurred on any of the four layers recorded with the crystal rotated about [011].

A zero-layer Weissenberg photograph around [001] taken with chromium radiation did not show any reflection of the above-mentioned set.

These observations strongly indicate that the five faint spots are not Bragg reflections but that they are explicable on the basis of the Renninger effect (see next paragraph).

The probable space group is thus  $O_h^7\text{-}Fd\bar{3}m$ .

#### Simulated reflections

According to the geometrical construction given by Renninger (1937), a reflection  $hkl$  can be simulated if the reciprocal-lattice point  $hkl$  lies upon the sphere of reflection simultaneously with a reciprocal-lattice point  $h_1k_1l_1$ . Both  $h_1k_1l_1$  and  $h_2k_2l_2$ , where  $h = h_1 + h_2$ ,  $k = k_1 + k_2$ , and  $l = l_1 + l_2$ , must be strong reflections. Inasmuch as the reflecting power extends over a region about a reciprocal lattice point, the Renninger phenomenon may be expected even when some very small rotation  $\Delta\varphi$  of the sphere is necessary to carry it from intersection with  $hkl$  to intersection with  $h_1k_1l_1$ .

Equations were set up to calculate all the reciprocal-lattice points  $h_1k_1l_1$  that touch the sphere of reflection simultaneously, or nearly so, with a point corresponding to a forbidden reflection  $hkl$ . Between six and nine  $h_1k_1l_1$  reflections were found for each forbidden reflection. For only those that were found to be of high intensity, additional calculations were carried out to determine the small rotation  $\Delta\varphi$  necessary to pass from the position of the reciprocal lattice at which  $hkl$  is in contact with the sphere to the position at which  $h_1k_1l_1$  is in contact. Each reciprocal-lattice point was hereby assumed to be the mathematical point, and the sphere of reflection was regarded as a mathematical sphere with the radius  $R = 1/\lambda$ , where  $\lambda = 1.54050 \text{ \AA}$ ,  $\text{Cu } K\alpha_1$ . The value of  $14.103 \text{ \AA}$  for the edge of the cubic

Table 1. *Simulated reflections*

| $hkl$  | $h_1k_1l_1$   | $h_2k_2l_2$   | $\Delta\varphi$                                      |
|--------|---|---|--|
| 420    | $\bar{2}26$ <i>vs</i>   | $60\bar{6}$ <i>vs</i>   | $0.75^\circ$   |
| 600    | $\begin{Bmatrix} 11,13,1 \\ 5,13,1 \\ 315 \end{Bmatrix}$ <i>s</i>         | $\begin{Bmatrix} \bar{5},\bar{1}\bar{3},\bar{1} \\ 11,\bar{1}\bar{3},\bar{1} \\ 3\bar{1}\bar{5} \end{Bmatrix}$ <i>s</i> | $\begin{Bmatrix} 0.06 \\ 0.04 \\ 0.37 \end{Bmatrix}$ |
|        |   |   |  |
|        |   |   |  |
| 820    | $226$ <i>vs</i>   | $60\bar{6}$ <i>vs</i>   | $0.44$   |
| 10,0,0 | $\begin{Bmatrix} 5\bar{1}3 \\ 13,11,3 \\ 12,12,4 \end{Bmatrix}$ <i>vs</i> | $\begin{Bmatrix} 51\bar{3} \\ \bar{3},\bar{1}\bar{1},\bar{3} \\ 2,\bar{1}\bar{2},4 \end{Bmatrix}$ <i>vs</i>             | $\begin{Bmatrix} 0.23 \\ 0.18 \\ 0.05 \end{Bmatrix}$ |
|        |   |   |  |
|        |   |   |  |
| 14,4,0 | $\begin{Bmatrix} \bar{3}93 \\ 5,15,5 \end{Bmatrix}$ <i>vs</i>             | $\begin{Bmatrix} 17,\bar{5},\bar{3} \\ 9,11,\bar{5} \end{Bmatrix}$ <i>vs</i>  | $\begin{Bmatrix} 0.09 \\ 0.08 \end{Bmatrix}$         |
|        |   |   |  |

$m$  = medium;  $s$  = strong;  $vs$  = very strong.

unit cell was used. Furthermore, it was assumed that the [001] direction coincides exactly with the rotation axis. The results given in Table 1 are in accord with the assumptions made above.

A simulated reflection can, of course, also be superimposed on a Bragg reflection and thereby cause its intensity to be too high. Such is believed to be true for instance for the 400 reflection. Its intensity measured on the second layer, with the crystal rotated about [011], appropriately corrected for the Lorentz and polarization factors was found to be approximately six times higher than that measured on the zero layer. The lower intensity value rather than an average value was therefore assigned to this reflection.

It seems reasonable to expect that for structures of large unit-cell dimensions, especially those incorporating heavy atoms, chances are great that some weak reflections may be represented with too high an intensity.

A quantitative evaluation of the phenomenon of simulated reflections has, of course, to be made with the application of the dynamical theory.

#### Intensity data

Intensity data for all the points accessible to the sphere of reflection for Cu  $K\alpha$  radiation were used for the refinement. These data were collected from Weissenberg photographs obtained by using the [011] direction of octahedral crystals (sample no. 1) as rotation axis. Since the identity period along this direction is only  $a_0/\sqrt{2}\text{\AA}$ , where  $a_0$  is the edge of the cubic unit cell, the complete sphere of reflections is in this way recorded with considerably fewer photographs than with the crystal rotated about [001]. This method, furthermore, yields cross correlations between even and odd layers not possible with the latter method for cubic face-centered structures.

The multiple-film technique of de Lange *et al.* (1939) and Robertson (1943) was used. A correction was made for the Lorentz and polarization factors but not for absorption or extinction. The diameter of the octahedral crystal used was 0.067 mm.

#### The trial structure

At the time the trial structure was worked out, sample no. 2 was not available. A trial structure was therefore derived to fit the assumption that the composition of the crystals corresponded approximately to the formula  $\text{ZrZn}_{14}$ . Since the density was not known, the number of atoms per unit cell was deduced from the atomic volumes. Assuming that these are not drastically altered by alloying the constituents, there have to be twelve  $\text{ZrZn}_{14}$  in the unit cell. If the space group  $Fd\bar{3}m$  is the correct one, such a structure cannot possibly be ordered since the point positions of lowest multiplicity in this space group are eight-fold. Several attempts were made to escape the acceptance of a disordered structure with a search for an alternative

origin for the five very weak spots interpreted as simulated reflections. Systematic consideration of ordered structures corresponding to the approximate composition  $\text{ZrZn}_{14}$  in other space groups disclosed, however, no plausible atomic arrangement.

The only reasonable trial structure that could be derived was such as to be closely related to the structure of  $\text{Mg}_3\text{Cr}_2\text{Al}_{18}$ , for which the atoms are arranged according to space group  $Fd\bar{3}m$  as follows (Samson, 1958):

$$\begin{array}{lll} 96\text{Al in } 96g & x, x, z \\ 48\text{Al in } 48f & x, 0, 0 \\ 16\text{Mg in } 16d & \frac{5}{8}, \frac{5}{8}, \frac{5}{8} \\ 8\text{Mg in } 8b & \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \\ 16\text{Cr in } 16c & \frac{1}{8}, \frac{1}{8}, \frac{1}{8} \\ x_g = 0.0666, z_g = 0.2998, x_f = 0.1407 \end{array}$$

The metallic radius of magnesium is very nearly the same as that of zirconium, which is about 1.60 Å. The effective metallic radii observed for the smaller aluminum and chromium atoms in various structures are comparable to the radius observed for zinc atoms, which varies around 1.35 Å in metallic structures.

In view of the relatively long nearest-neighbour distances around position  $8b$ , it seems most likely that this position is exclusively or at least predominantly occupied by zirconium atoms. The configuration of atoms around the position  $16d$  is such as to provide a volume somewhat smaller than that around  $8b$ , but still appropriate for large zirconium atoms. This position  $16d$  seems to be the one best adapted in this structure for a disordered arrangement of zirconium and zinc atoms with metallic radii differing by about fifteen percent from one another. Hence, if the composition  $\text{ZrZn}_{14}$  found for the octahedral crystals is approximately correct, it seems reasonable to assume that there are eight zirconium atoms in  $8b$ , about four zirconium atoms and twelve zinc atoms (possibly some vacancies) in  $16d$ , and 160 zinc atoms in the positions  $96g$ ,  $48f$ , and  $16c$ . This atomic arrangement corresponds to the composition  $\text{ZrZn}_{14.3}$  and an X-ray density of  $\rho = 7.30 \text{ g.cm.}^{-3}$ , if no allowance is made for vacancies.

The experimental results obtained from sample no. 2 as described in the section Composition and density, correspond very nearly to an ordered atomic arrangement with eight zirconium atoms in the  $8b$  position and 176 zinc atoms in the positions  $96g$ ,  $48f$ ,  $16d$ , and  $16c$ . Such a structure corresponds exactly to the composition  $\text{ZrZn}_{22}$  and a calculated density of  $\rho = 7.24 \text{ g.cm.}^{-3}$ . The measured value is  $\rho = 7.15 \pm 0.05 \text{ g.cm.}^{-3}$ .

In view of the small quantity of crystals available in sample no. 1 for chemical analysis it is possible that the composition  $\text{ZrZn}_{14}$ , although in accord with that found by Chiotti and Kilp (1959), is incorrect. The result obtained from sample no. 2,  $\sim\text{ZrZn}_{22}$ , is with respect to the large quantity of sample used very reliable. Both compositions will therefore be considered

possible for the octahedral crystals of sample no. 1 used in the diffraction work.

The two alternatives may be comprehended with the aid of Table 2.

Two sets of structure factors were calculated, one with atoms placed according to Column *A* in Table 2,  $\text{ZrZn}_{14.3}$ , the other with the atoms placed according to Column *B* in Table 2,  $\text{ZrZn}_{22}$ . The positional parameters chosen for this calculation were those obtained for the  $\text{Mg}_3\text{Cr}_2\text{Al}_{18}$  structure. Both sets of structure factors agreed well with the observed ones obtained from the octahedral crystals of sample no. 1.

### Refinement of the structural parameters

Several least-squares refinements such as described by Hughes (1941) were carried out with the use of all intensity data obtainable with  $\text{Cu } K\alpha$  radiation. The calculations were carried out on the 205 Datatron computer with a program written by Dr Herbert Segall for cubic space groups. With this program the positional parameters as well as individual temperature factors for each atom and an overall scale factor are optimized. The  $F_o$  values with weights similar to those of Hughes (1941) were taken as observational quantities. The most intense reflection 880 was given zero weight, and a number of other very strong reflections that were feared to be weakened by extinction effects were given a lowered weight. The atomic form factors listed in *Internationale Tabellen*, Bd. II (1935), were employed, 'corrected' for anomalous dispersion according to Dauben and Templeton (1955). A preliminary scale factor and an overall temperature factor to be used at the start of the refinement were evaluated from a semilogarithmic plot.

One hundred thirty-seven observational equations were set up and reduced to a set of six equations, that were solved for the scale factor and the five temperature factors. Only those off-diagonal terms connecting the temperature factors with the scale factor were included in the matrix. The normal equations for the three positional parameters were

solved separately. For these, the off-diagonal matrix elements were not calculated.

Two separate least-squares refinements were carried out in parallel, one for each of the two alternatives given in Table 2. Both refinements were recycled until the shifts in the positional parameters were less than 0.001 Å and the changes in the individual temperature factors averaged about three percent.

### Interpretation of the refined parameters

The refined positional parameters and temperature factors for the two alternatives *A* and *B* are listed in Table 2. The positional parameters for both cases came out to be identical. Such was also the case with the standard deviations given in the same table.

The only difference in the two results is that in the temperature factor for the atoms in the position 16*d*. The overall scale factor was influenced by less than one percent. The higher temperature factor obtained in *A* is, of course, compensating for the slightly larger scattering factor used.

In view of the similarity between the temperature factors in Column *B*, Table 2, one may feel that these values are more attractive. On the other hand, a random distribution of the large zirconium atoms and the small zinc atoms in the position 16*d* may be expected to have an effect similar to that of thermal vibration of large amplitude, such as is indicated by the large temperature factor in Column *A*, Table 2. Another complicating factor in the interpretation of the temperature factors is the possibility of vacancies; for instance, with ten zinc atoms, four zirconium atoms and two vacancies in 16*d* the average number of electrons per site corresponds very nearly to the scattering power of one zinc atom per site. Consequently, the refined parameters obtained by assuming a completely ordered structure,  $\text{ZrZn}_{22}$ , Column *B*, are very nearly identical with those corresponding to a disordered structure of the composition  $\text{ZrZn}_{14.2}$  including two vacancies in 16*d*.

The overall agreement between the observed and

Table 2. *Refined positional parameters and temperature factors*

Origin of coordinates at  $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$  from center ( $\bar{3}m$ )

| Kind and number of atoms         |                    | Point positions   | Positional parameter                               | Temperature factor ( $\text{\AA}^2$ ) |  |
|----------------------------------|--------------------|---|--|---------------------------------------|--|
| $\text{ZrZn}_{14.3}$             | $\text{ZrZn}_{22}$ |   |  | $\text{ZrZn}_{14.3}$                  | $\text{ZrZn}_{22}$<br>or<br>$\text{ZrZn}_{14.2}^*$ |
| <i>A</i>                         | <i>B</i>           |   |  | <i>A<sub>a</sub></i>                  | <i>B<sub>b</sub></i>                               |
| 96 $\text{Zn}_g$                 | 96 $\text{Zn}_g$   | ( <i>g</i> ) $x, x, z$ , etc.                               | $x = 0.0630 \pm 0.0003$<br>$z = 0.3055 \pm 0.0003$ | 0.37                                  | 0.38   |
| 48 $\text{Zn}_f$                 | 48 $\text{Zn}_f$   | ( <i>f</i> ) $x, 0, 0$ , etc.                               | $x = 0.1400 \pm 0.0003$                            | 0.42                                  | 0.41   |
| 12 $\text{Zn}_d + 4 \text{Zr}_d$ | 16 $\text{Zn}_d$   | ( <i>d</i> ) $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$ , etc. |  | 0.72                                  | 0.46   |
| 8 $\text{Zr}_b$                  | 8 $\text{Zr}_b$    | ( <i>b</i> ) $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ , etc. |  | 0.13                                  | 0.12   |
| 16 $\text{Zn}_c$                 | 16 $\text{Zn}_c$   | ( <i>c</i> ) $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$ , etc. |  | 0.52                                  | 0.49   |

\* If 10  $\text{Zn} + 4 \text{Zr} + 2$  vacancies in 16*d*.

calculated structure factors is equally good for the two cases *A* and *B*. The X-ray diffraction data do not therefore discriminate between a disordered structure corresponding to the approximate composition  $\text{ZrZn}_{14}$  and an ordered structure corresponding to  $\text{ZrZn}_{22}$ . If the variation in the composition found by chemical analysis is real it indicates a composition range that extends from approximately six percent to nine percent of zirconium by weight. The degree of ordering in the crystals will then depend upon the experimental parameters such as annealing time, temperature, and pressure.

Table 3. *Calculated and observed structure factors*

The column headings are  $k$ ,  $l$ ,  $F_c$  and  $F_o$ . The  $F_o$  are obtained from octahedral crystals of sample no. 1 (see text)

[illegible]

The calculated structure factors given in Table 3 are those obtained with the atoms placed according to Column *B*, Table 2. The reliability factor is  $R=14.8$  for all observed reflections and  $R=12.4$  if the strongest reflections weakened by extinction are not included.

The interatomic distances are listed in Table 4. In calculating the standard deviations also given in this table the functional dependence of the distances on

the positional parameters was taken properly into account.

### Description of the structure

The present phase represents a structure of a type closely related to that of the  $\text{Mg}_3\text{Cr}_2\text{Al}_{18}$  phase, which has previously been described and illustrated in four figures (Samson, 1958). Below is given a brief description of the structure in a version somewhat different from that used before.

At ( $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ ) there is a group of six zinc atoms (48f) located at the vertices of a regular octahedron. Outside this group of atoms there are four zinc atoms (16c) at the vertices at a regular tetrahedron. Each of these atoms is shared between two such 10-atom complexes. At ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ) there is a zirconium atom (8b) surrounded by a shell of twelve zinc atoms (96g) forming a truncated tetrahedron, bounded by four hexagons and four equilateral triangles. Out from the centers of the four hexagonal faces there are four atoms (16d, Zr and/or Zn) located at the vertices of a regular tetrahedron. Each of these atoms is shared between two such 17-atom complexes.

The structure can now be described as an NaTl type structure with the 10-atom complexes in place of the sodium atoms and the 17-atom complexes in place of the thallium atoms. Each group of atoms is accordingly surrounded by four groups of the same kind and four groups of the other kind.

## Discussion of the structure

## General

An interesting feature of this structure is the uniquely large stoichiometric ratio between zirconium and zinc, which in the case of complete ordering is 1:22. Such a ratio has not been reported for any other metallic structure. Paine and Carrabine (1960) reported the existence of three compounds of the approximate composition  $MeBe_{20}$ , where  $Me$  represents molybdenum, rhenium, or tungsten. Their powder data indicate a cubic unit cell of  $a_0 = 11.6 \text{ \AA}$  and the space group  $O_h^1-Fd\bar{3}m$  or  $T_h^1-Fd\bar{3}$ . A cursory examination made by the author showed that 176 beryllium atoms and 8  $Me$  atoms can be accommodated in the unit cell in the same fashion as for  $ZrZn_{22}$ . Structure factor calculations have, however, not been made.

The contrasts in the ligancies of the crystallographically different atoms will be set forth in the following discussion of the coordination polyhedra observed.

### *The coordination polyhedra and packing of atoms*

The ligation of atoms around the eight zirconium atoms  $Zr_b$  produces a coordination polyhedron with sixteen vertices and twenty-eight triangular faces that occurs in the A12, C14, C15, and C36 structures and in the more complex structures  $Mg_{32}(Al, Zn)_{49}$  (Bergman, *et al.*, 1957) and  $Mg_3Cr_2Al_{18}$  (Samson, 1958).

This coordination polyhedron, which for the sake of brevity is referred to as the Friauf polyhedron,\* may be described as a truncated tetrahedron bounded by four equilateral triangles and by four hexagons out from the centers of which there are four atoms located at the vertices of a regular tetrahedron. Other Friauf polyhedra with a zirconium atom at the center are observed in the structures  $\text{ZrZn}_2$ ,  $\text{ZrFe}_2$ , and  $\text{ZrCo}_2$ , which are all of the C15 type. While in these structures the atoms at the vertices of the regular tetrahedron are zirconium atoms, in the  $\text{ZrZn}_{22}$  structure they consist of zinc atoms. The distance observed between the central zirconium atom and these four vertices in the  $\text{ZrZn}_{22}$  structure, 3.054 Å, is accordingly less than that observed in the  $\text{ZrZn}_2$  structure, 3.203 Å. The distance between the central zirconium atom and the twelve zinc atoms at the vertices of the truncated tetrahedron is  $3.017 \pm 0.005$  Å. The weighted average of the distances between the zinc atoms at the vertices of the truncated tetrahedron is 2.586 Å in this structure, 2.614 Å in the  $\text{ZrZn}_2$  structure (C15 type), and 2.594 Å in the  $\text{MgZn}_2$  structure (C14 type). Hence, the overall size of the truncated tetrahedron in these three structures, although they represent different types, is very nearly the same. When these zinc atoms are replaced by iron or cobalt atoms the overall size of the truncated tetrahedron decreases, as is indicated by the corresponding averaged distances for  $\text{ZrFe}_2$  and  $\text{ZrCo}_2$ , which are 2.49 Å and 2.42 Å respectively.

The atoms in the position 16d are next to be considered. In the completely ordered structure they consist of zinc atoms. The coordination polyhedron around them is an approximately hexagonal prism with nearly square prism faces, and with its extended axis passing through two zirconium atoms  $\text{Zr}_b$ . These prisms are formed by the six-sided faces of two adjacent truncated tetrahedra and have accordingly zinc atoms  $\text{Zn}_g$  at their vertices. Around each Friauf polyhedron a set of four such prisms is arranged with their centers, occupied by  $\text{Zn}_d$  atoms, at the vertices of a regular tetrahedron. The average edge of the prism is 2.629 Å. With twelve spheres of equal size in contact with one another at the vertices of an idealized hexagonal prism of edge 2.63 Å with square prism faces a sphere twenty percent larger in radius can be accommodated at the center of the prism. The packing of atoms around the  $\text{Zn}_d$  atoms seems to be rather loose.

The coordination shell around the  $\text{Zn}_g$  atoms may be described as an approximately pentagonal prism with ten zinc atoms at the vertices and two atoms,  $\text{Zn}_c$  and  $\text{Zr}_b$ , on the approximately pentagonal axis. The coordination shell around the  $\text{Zn}_f$  atoms is very similar to that just described. Both  $\text{Zn}_g$  and  $\text{Zn}_f$  have thus coordination number twelve. The packing appears to be of normal efficiency.

The coordination polyhedron around each zinc atom

in the position 16c may be described as an icosahedron compressed in the direction of one of the three-fold axes. Six of the zinc atoms  $\text{Zn}_f$  at the vertices of the distorted icosahedron are accordingly at a shorter distance, 2.502 Å, and six,  $\text{Zn}_g$ , at a longer distance, 2.831 Å, from the central zinc atom. The average value of these distances is 2.667 Å. On the basis of considerations similar to those mentioned in an earlier paper (Samson, 1958) it can be concluded that the packing around the zinc atoms in the position 16c is very close, most likely closer than that achievable by close packing of spheres of equal size. Similar icosahedral  $\text{ZnZn}_{12}$  complexes occur in the  $\text{D}_{2d}$  type structures  $\text{MeZn}_{13}$  ( $\text{Me} = \text{Na}, \text{K}, \text{Ca}, \text{Sr}, \text{Ba}$ ) and furthermore in the structure of  $\text{Mg}_2\text{Zn}_{11}$  (Samson, 1949). In these structures the icosahedra are deformed in a different way as described above for  $\text{ZrZn}_{22}$ . It is, however, interesting to see that the distance between the central zinc atom and the twelve zinc atoms at the vertices of each icosahedron in the  $\text{NaZn}_{13}$  structure, which has been very carefully refined by Shoemaker, *et al.* (1952), is 2.659 Å, and hence very nearly the same as the average distance observed for the deformed icosahedron in  $\text{ZrZn}_{22}$ , which is 2.667 Å. The weighted averages of the distances between the vertices are also very nearly the same, 2.797 Å for  $\text{NaZn}_{13}$  and 2.812 Å for  $\text{ZrZn}_{22}$ . The possible significance of these figures will be discussed in a later section. The  $\text{Mg}_2\text{Zn}_{11}$  structure unfortunately has not been refined by modern methods to yield distances of sufficient accuracy for comparison.

#### *The bond distances and their interpretation*

The interatomic distances are listed in Tabel 4. The bond numbers as well as the calculated valences also given in this table have been derived by the application of the equation  $D_n = D_1 - 0.600 \log_{10} n$  (Pauling, 1947). The single-bond radius assigned to each metal atom is such as to be consistent with the valence calculated for that atom (Pauling, 1949, 1960).

The analysis given above of the coordination polyhedra reveals a variation in the efficiency of the packing of atoms around the crystallographically different zinc atoms. These relative efficiencies have been indicated in Table 4 as normal for  $\text{Zn}_g$  and  $\text{Zn}_f$ , low for  $\text{Zn}_d$  and very high for  $\text{Zn}_c$ . These properties may be related to the valences and single bond radii in a way as was done by Pauling (1947) for manganese (see p. 546 *loc. cit.*). Applying those arguments to this structure one may say that the  $\text{Zn}_g$  and  $\text{Zn}_f$  atoms have a normal metallic valence and corresponding normal size, the  $\text{Zn}_d$  atoms a smaller valence and larger size, and the  $\text{Zn}_c$  atoms a higher valence and smaller size. Such size relationships are made very obvious by comparison of certain isomorphous structures with one another, as for instance this structure and the  $\text{Mg}_3\text{Cr}_2\text{Al}_{18}$  structure. The large  $\text{Zn}_d$  atoms take the places of two-thirds of the magnesium atoms, which have a metallic radius about fifteen

\* It was first observed in the  $\text{MgCu}_2$  and  $\text{MgZn}_2$  structures determined by Friauf (1927a, b).

Table 4. *Interatomic distances, bond numbers and calculated valences*

| Kind of atom | Ligancy   | Distance (Å)       |  | Bond number $n$ | Calculated valence $v$ and single bond radius $R(1)$ | Coordination polyhedron   | Packing efficiency |
|--------------|-----------|--------------------|--|-----------------|--|---|--------------------|
| $Zr_b$       | 12 $Zn_g$ | $3.017 \pm 0.005$  |  | $0.260$         | $v=4.21$<br>$R(1)=1.437$                             | Friauf polyhedron   | Normal             |
|              | 4 $Zn_d$  | $3.054 \pm <0.001$ |  | $0.273$         |  |   |                    |
|              | 16        |                    |  |                 |  |   |                    |
| $Zn_d$       | 12 $Zn_g$ | $2.959 \pm 0.005$  |  | $0.178$         | $v=2.69$<br>$R(1)=1.279$                             | Approx. hexagonal prism with two $Zr_b$ atoms at the extended approx. hexagonal axis        | Low                |
|              | 2 $Zr_b$  | $3.054 \pm <0.001$ |  | $0.273$         |  |   |                    |
|              | 14        |                    |  |                 |  |   |                    |
| $Zn_g$       | 2 $Zn_g$  | $2.623 \pm 0.009$  |  | $0.531$         | $v=3.94$<br>$R(1)=1.229$                             | Approx. pentagonal prism with two atoms, $Zn_c$ and $Zr_b$ , at the approx. pentagonal axis | Normal             |
|              | 2 $Zn_g$  | $2.941 \pm 0.009$  |  | $0.157$         |  |   |                    |
|              | 1 $Zn_g$  | $2.512 \pm 0.014$  |  | $0.816$         |  |   |                    |
|              | 2 $Zn_f$  | $2.831 \pm 0.005$  |  | $0.240$         |  |   |                    |
|              | 1 $Zn_f$  | $2.666 \pm 0.006$  |  | $0.451$         |  |   |                    |
|              | 1 $Zn_c$  | $2.831 \pm 0.005$  |  | $0.203$         |  |   |                    |
|              | 1 $Zr_b$  | $3.017 \pm 0.005$  |  | $0.260$         |  |   |                    |
|              | 2 $Zn_d$  | $2.959 \pm 0.005$  |  | $0.178$         |  |   |                    |
|              | 12        |                    |  |                 |  |   |                    |
| $Zn_f$       | 2 $Zn_g$  | $2.666 \pm 0.006$  |  | $0.451$         | $v=4.40$<br>$R(1)=1.229$                             | Approx. pentagonal prism with two $Zn_c$ atoms at the approx. pentagonal axis               | Normal             |
|              | 4 $Zn_g$  | $2.831 \pm 0.005$  |  | $0.240$         |  |   |                    |
|              | 4 $Zn_f$  | $2.793 \pm 0.006$  |  | $0.277$         |  |   |                    |
|              | 2 $Zn_c$  | $2.502 \pm <0.001$ |  | $0.716$         |  |   |                    |
|              | 12        |                    |  |                 |  |   |                    |
| $Zn_c$       | 6 $Zn_f$  | $2.502 \pm <0.001$ |  | $0.716$         | $v=5.51$<br>$R(1)=1.186$                             | Icosahedron   | Very high          |
|              | 6 $Zn_g$  | $2.831 \pm 0.005$  |  | $0.203$         |  |   |                    |
|              | 12        |                    |  |                 |  |   |                    |

percent larger than that of the aluminum atoms and a small valence ( $v=2$ ); the small  $Zn_c$  atoms take the places of the chromium atoms with a metallic radius about ten percent smaller than that of aluminum atoms and a high metallic valence ( $v \sim 5$ ); and finally the  $Zn_g$  and  $Zn_f$  atoms take the places of all the aluminum atoms, which are intermediate in both size and valence. One is led to conclude that the zinc atoms are of different kinds in the chemical sense as well as in the crystallographic sense. The  $ZrZn_{22}$  phase may accordingly be regarded as a quaternary compound of the kind  $Zr^{+4}Zn_2^{+3}Zn_2^{+5}Zn_{18}^{+4}$ , where the superscripts indicate the approximate metallic valences. The uniquely large stoichiometric ratio between zirconium and zinc becomes on such considerations very plausible. The interpretation in terms of metallic valences and atomic sizes is unfortunately bound to be highly qualitative. One reason is the uncertainty in the occupancy of the position 16*d*. Another reason will be given below.

#### Compressional strain

The icosahedral configuration of the twelve zinc atoms,  $6Zn_g + 6Zn_f$ , around the zinc atom in the 16*c* position results in six short bonds  $Zn_c-6Zn_f=2.502$  Å, and six long bonds  $Zn_c-6Zn_g=2.831$  Å as has been pointed out in a previous section. One may be led to assume that this type of bonding is related to the bonding properties in the zinc metal, where each zinc atom forms six short bonds of 2.660 Å and six long bonds of 2.907 Å. Icosahedra almost identical to that observed in  $ZrZn_{22}$  are however the  $CrAl_{12}$  icosahedra

observed in the  $Mg_3Cr_2Al_{18}$  structure and the  $VA_{12}$  icosahedra observed in  $\alpha(V-Al)$  Brown (1956). In a discussion of 'abnormally short contacts between a transition metal atom and some of the surrounding Al atoms' Taylor (1954, 1958) considered the possibility that such very short bond distances are associated with electron transfer. In all three structures quoted above, however, the atomic arrangement is such that not even a large shift of the atom in the 48*f* position, which has only one degree of freedom, can alleviate the shortness of the  $Zn_c-Zn_f$  bonds,  $Cr_c-Al_f$  bonds, and  $V_c-Al_f$  bonds, respectively; and as such a large shift would necessarily lead to excessively long and short  $Zn_f-Zn_g$  or  $Al_f-Al_g$  distances it seems possible that the six short bonds are under compression and the six longer bonds under tension. The small functional dependence of these short distances on the positional parameter for  $Zn_f$ , or  $Al_f$  respectively, is also reflected in the small probable error for these distances (Table 4). The weighted average of the twelve distances between the  $Zn_c$  atom and the vertices of the icosahedron, 2.667 Å, corresponds indeed very nearly to the valence 5 obtained for the corresponding atom in the  $NaZn_{13}$  structure. It seems therefore possible that the valence 5.5 obtained here is too high.

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## Classification of Symmetry Groups

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Point groups and space groups in 3-D are two classes of symmetry groups that have proved most useful in crystallography. Recently other sorts of groups have been described involving a change of 'side', sign (antisymmetry), or color; and some of these have already been applied to problems of twinning and magnetic structures. A uniform classification of these various groups should help in visualizing the relations among them and in working out new applications.

If all variables are treated geometrically, including antisymmetry, symmetry groups may be classed according to the dimensions of space that are invariant under their operations. Thus the 80 'antisymmetry groups in a plane' have 2-D and 3-D spaces invariant. The group is 'in' the highest dimensional space of invariance, and translations are allowed only in the lowest dimensional space. But spaces of intermediate dimensions may also be invariant: the 31 'Streifenornamente' have 1, 2, 3 spaces invariant. Alternatively these classes may be described by the symmetry of the invariant space, using the continuous translations and rotations. Thus the class of groups in 2, 3 space are all the crystallographic subgroups of  $t\infty/mm$ , and class 1, 2, 3 are all subgroups of  $tmmm$ .

All such classes through 4-D are tabulated.

### Introduction

After the classical descriptions of crystallographic lattices and space groups in the nineteenth century, it was generally considered that everything had been said on the subject. There was a revival of interest about 1930 when several papers appeared in the *Zeitschrift für Kristallographie* describing line groups, plane groups, three-dimensional groups in four dimensions, continuous groups, and so on. These esoteric matters were soon forgotten, but ever since the appearance in 1951 of Schubnikov's book on anti-symmetric point groups, the field has blossomed. Antisymmetry is a beautifully simple idea that has moreover proved useful in solving magnetic structures and other problems. Symmetry groups are now generally classified in terms of antisymmetry or extensions

of that idea (Zamorzaev & Sokolov, 1957; Mackay, 1957; Niggli, 1959; Nowacki, 1960). It is the single purpose of this paper to recall and develop another aspect of symmetry groups that can serve as a basis of classification. I refer to the space—point, plane, line, cell, or some combination of them—that is invariant under all operations of the symmetry groups in a class. The dimensions of the space, or its general symmetry, is a description of the class of groups. With this alternate viewpoint, groups are more easily described for some purposes.

### Antisymmetry and dimensions

I take as point of departure the paper by Heesch (1930a), 'Über die vierdimensionalen Gruppen des dreidimensionalen Raumes'. These groups are in fact